Local structural properties in nanocrystals $CeAl_2$, $CePt_2$ and $CePt_{2.5}$

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Abstract

When antiferromagnetic $CeAl_2$, $CePt_2$ and $CePt_{2.5}$ crystallites are reduced to nanometer scale particle sizes, their physical properties become that of a nonmagnetic Kondo system. Although particle size likely plays a dominant role, structural changes between the bulk and nanoscale particles may also play an important role. Since the small particle sizes limit the utility of diffraction experiments, the local structural properties of bulk and nanocrystalline $CeAl_2$, $CePt_2$ and $CePt_{2.5}$ samples were studied by x-ray absorption fine structure measurements (XAFS) at the Ce and Pt L_3-edges. In $CeAl_2$, the XAFS studies show that the nanocrystalline material is severely disordered compared to its bulk counterpart and that the nearest-neighbor Ce-Al bond length is about 0.4 Å shorter in the nanocrystal than in the bulk. In $CePt_2$ and $CePt_{2.5}$, we also find that the local structure in the nanocrystals has a large amount of disorder/distortion from all atom sites and that the Ce atom is in a mixed valence state between Ce^{3+} and Ce^{4+}. These observations strongly suggest that in addition to size and surface effects, structural disorder plays a role in determining the Kondo behavior in these nanocrystals.

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I. INTRODUCTION

1)Describe the studies on $CeAl_2$.

2)Describe the studies on $CePt_{2+x}$.

The antiferromagenitcally ordering temperaure in $CePt_2$ is known at $T_N \simeq 2$ K[4–7]. As the particle size is in a nanometer scale, the T_N moves toward to further low temperature[3].

The effect of particle size on physical and electronic properties has attracted broad interest with many studies reported on this subject, both experimentally and theoretically[2]. The $CeAl_2$, $CePt_2$ and $CePt_{2.5}$ display the fascinating property that as its particle size becomes comparable to the nanometer scale, the system transitions from displaying magnetic order to Kondo behavior. This transition has been explained in terms of size and surface effects[3]. However, structural changes in the nanosize crystals may also be relevant. We explored this possibility through local structure measurements of bulk and nanocrystalline $CeAl_2$, $CePt_2$ and $CePt_{2.5}$ using the x-ray absorption fine-structure technique (XAFS) which can detect both the bond length and the disorder of a near-neighbor atomic pair from a selected atom species. In addition, we can obtain the electronical properties of $4f$-valance state from the x-ray absorption measurements at the Ce L_3-edege.

For the XAFS measurements, the bulk samples $CeAl_2$, $CePt_2$ and $CePt_{2.5}$ were fabricated by arc melting and the $\sim$80 Å diameter nanocrystals were obtained using a liquid-nitrogen cold trap[3]. The crystals were ground and sieved through a 25 μm sieve. The sieved powder was uniformly spread over adhesive tape which was folded several times to obtain the absorption edge step of $0.3 - 1.0$. Transmission Ce and Pt L_3-edge (5724 and 11564 eV, respectively) XAFS measurements from $CeAl_2$ and $CePt_{2.5}$ at $T = 20$ K were made at beamline 2-3 of the Stanford Synchrotron Radiation Laboratory (SSRL) and the measurements on $CePt_2$ were done at the PNC-CAT of the Advanced Photon Source (APS) using a 1/2(SSRL) and 1/4(APS)-tuned Si(111) double monochromator.

Figure 1 shows the normarized total x-ray absorption (μx) from $CeAl_2$ (a) and $CePt_2$ (b) at Ce L_3-edge as a function of incident x-ray energy. The relatively sharper white line from the nano crystal indicates narrowing energy band due to the nano crystal size. More interesting feature is found in (b), which is measured on $CePt_2$. There is an obvious peak existing in the nanocrystal data just after the absorption edge. We find the same feature

from the $CePt_{2.5}$ nanocrystals. In the $2p$-$5d$ electron transition under the mixed states of Ce^{3+} ($4f^1 5s^1$) and Ce^{4+} ($4f^0 5s^2$), the strange shape above the post-absorption edge has been studied by Sham *et al.*[13] Our observation strongly suggests that the Ce atom has the mixed state of Ce^{3+} and Ce^{4+}. We will discuss this with the structural properties later in detail.

The oscillation part in the post-edge has been well-known as the XAFS modulation which is directly related to the atomic local structure[8]. The XAFS was analyzed with the UWXAFS package[9] (methods are described elsewhere[10]), using the photoelectron back scattering functions calculated with the FEFF8 code[11]. After the atomic background was substracted from the raw data using the AUTOBK which is a part of the UWXAFS package, the XAFS modulation (χ) was obtained. Figure 2 shows the XAFS from $CeAl_2$, $CePt_2$ and $CePt_{2.5}$ nanocrystals and their bulk countparts at Ce and Pt L_3-edges. The weak intensity of the XAFS data indicates that the local structures in the nanocrystals are considerably disorder, comparing with those in their bulk countparts. We analyzed the XAFS in r-space after the XAFS data from L_3-edge within $2.7 - 7.5$ Å^{-1} and $2.5 - 9.5$ Å^{-1} for the nano and bulk specimens, respectively, were Fourier transformed. For the Fourier transformat, the Hanning window with the window sills of 0.5^{-1} was used.

Figure 3 shows the magnitude of Fourier transformed XAFS data from bulk and nanocrystalline samples of $CeAl_2$. Note that the peaks are shifted on the $\tilde{r}$ axis from their true bond lengths due to the phase shift of the back scattered photoelectron. Detailed fits are therefore necessary to obtain quantitative information. Fits to the bulk data start from the $C15$ Laves structure (space group ($fd\bar{3}m$)), allowing the bond length and the Debye-Waller factor (σ^2, including thermal vibrations and static disorder) for each shell below 7 Å to vary. The fitting paramers are summarized in Table I. We find that the Ce atoms have 12 Al neighbors at 3.356 ± 0.005 Å and 4 Ce neighbors at 3.503 ± 0.006 Å. The σ^2s are 0.0038 ± 0.0004 Å^2 for the Ce-Al pairs and 0.0021 ± 0.0007 Å^2 for the Ce-Ce pairs, respectively. These small σ^2s suggest that the crystalline structure is well ordered. We derive a lattice constant of 8.095 ± 0.015 Å from these data, roughly consistent with the previous x-ray diffraction measurement of 8.054 Å[12].

The nanoparticle fits also start from the bulk model, but reliable results are only obtained from shells shorter than 3.5 Å. The inset shows the various fits assuming that only aluminum, only oxygen, or mixed Al and O occupy the Al site. The models using only Al or only O do not fit the measured data satisfactorily. The fit is considerably improved by including

about 10 ± 5% oxygen into the Al site. This observation of oxygen in the Al site agrees with the previous study[3]. In any case, these results strongly suggest that the Al site is partially occupied by oxygen. The best fit shows that the bond lengths are 2.44 ± 0.03 Å and 2.96 ± 0.02 Å for Ce-O and Ce-Al pairs, respectively. The σ^2s in the nanoparticles are 0.044 ± 0.014 Å^2 for 11 ± 5 of aluminum neighbors and 0.005 ± 0.009 Å^2 for 1.3 ± 0.9 of oxygen neighbors. The average σ^2 of the Ce-Al and Ce-O pairs is about an order of magnitude larger than that of the Ce-Al pair in the bulk and the bond length of Ce-Al is about 0.4 Å shorter than the bond length of Ce-Al in the bulk. These measurements indicate that both large distortions and intrinsic disorder exist around Ce in the nanocrystals compared to the bulk.

In the analysis of the $CePt_2$ and $CePt_{2.5}$ XAFS data, we have used the same method as mentioned above. In the $CePt_{2.5}$, the disordered $C15$ structure where the extra Pt randomly spreads onto all Ce sites[4] was started. Figure 4 shows the ampulitude of XAFS from $CePt_{2.5}$ crystals at Ce L_3-edge (a) and Pt L_3-edge (b). The XAFS data shown in Fig. 2 within 2.7 − 8.0 and 2.7 − 9.5 Å^{-1} for nano and bulk samples, respectively, were Fourier transformed. From the ananysis on the bulk sample, we find the lattice constant of 7.71 ± 0.05 Åwhich agrees well with the study by Lawrence *et al.*[4]. With a fully occupied model, the analysis shows that 12 Pt and 4 Ce atoms are located at 3.175 ± 0.008 Åand 3.439 ± 0.007 Å, respectively. The σ^2 are 0.013 ± 0.001 and 0.003 ± 0.001 Å^2 for the Ce−Pt and Ce−Ce pairs, respectively. From this local structural studies, we find that the bond lengths of Ce−Pt is is about 0.02 Å shorter while the Ce−Ce pairs has about 0.1 Å longer bond length than those in the crystalline symmetry. The fit parameters are summarized in Table II.

The XAFS data from the nanocrystals were also analyzed with assuming the same crystalline structure of the disordered $C15$ crystalline symmetry. The data in Fig. 4 (a) are the Fourier transformed amplitude of the data in Fig. 2 within the k-range of 2.7 − 8.0 Å^{-1}. A satisfactory fit can be obtained with a mix model of Ce and O for the nearest neighbor. The fit shows that 15 ± 5 % of oxygen is occupied at the Pt site. The bond lenght of Ce−O and Ce−Pt pairs are 2.39 ± 0.02 and 2.843 ± 0.007 Åwith σ^2s of 0.021 ± 0.001 Å^2 Because of the high correlation of the σ^2s between Ce−O and Ce−Pt pairs, a single σ^2 was used for the both pairs in the fit. In the conjecutive neighbors, 4 Ce−Ce, 16 Ce−Pt and 12 Ce−Ce pairs have the bond lengths of 3.29(1), 4.46(2) and 5.03(2) Å with σ^2 of 0.024(2), 0.028(4) and 0.021(3) Å^2, respectively. The analysis shows that the bond lengths in the nanocrystals

are about 4−5 Å shorter than those in the bulk and the σ^2s are about 1.5−2 times larger than those in the bulk countpart.

Figure 4 (b) shows that the XAFS data from $CePt_{2.5}$ at Pt L_3-edge. Unlikely Ce L_3-edge, we do not observe a special difference at the near edge which is not shown here. The data were Fourier transformed from the data in Fig. 2 within the k-range of $2.5 - 14.5$ Å^{-1} and $2.5 - 11.5$ Å^{-1} for the bulk and nano specimens, respectively. The analysis the data for the bulk was started with the crystalline symmetry mentioned above. The bond lengths and σ^2s of the atomic pairs are summarized in Table II.

II. CONCLUSIONS

we have studied the local structural properties of nanocrystalline $CeAl_2$, comparing with its bulk counterpart. A substantial amount of disorder in the nanoparticle is observed and the Ce-Al bond length is shorter than that in the bulk. Moreover, oxygen is observed in the Al site. These changes in the structural properties should be included in any proper theory of the changes in the physical properties of nanocrystalline $CeAl_2$.

Acknowledgments

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TABLE I: Results of least-squares fit at Ce L_3-edge from $CeAl_2$ at 20 K. The total number of data points in the Fourier tranformed XAFS is determined by Stern's rule[9]; $(2\Delta k\Delta r\ /\ \pi\ +\ 2)$ where Δk is the region of k in which the data were used for Fourier transform into r-space and Δr is the fit region.

Sample	χ^2_ν	r-factor	$N_{\rm I}$	ν	S_0^2
Nano	12.4	0.0067	9	4	0.98 ± 0.10
Bulk	240.5	0.0105	29	16	0.90 ± 0.06

TABLE II: Bond lengths and σ^2s in $CePt_2$ and $CePt_{2.5}$ determined at Ce and Pt L_3-edges at 20 K

	Ce L_3-edge				Pt L_3-edge			
	Ce−Pt		Ce−Ce		Pt−Pt		Pt−Ce	
Specimen	r(Å)	σ^2(Å^2)	r(Å)	σ^2(Å^2)	r(Å)	σ^2(Å^2)	r(Å)	σ^2(Å^2)
$CePt_2$(bulk)	3.18(1)	0.012(1)	3.43(1)	0.012(1)	2.723(1)	0.0015(1)	3.19(1)	0.013(1)
$CePt_2$(nano)	2.91(1)	0.018(2)	3.37(1)	0.025(2)	2.690(5)	0.0051(2)	2.86(5)	0.050(8)
$CePt_{2.5}$(bulk)	3.17(1)	0.014(1)	3.44(2)	0.0030(9)	2.714(1)	0.0019(1)	3.11(1)	0.014(1)
$CePt_{2.5}$(nano)	2.84(1)	0.021(1)	3.29(1)	0.026(2)	2.690(3)	0.0054(3)	2.99(7)	0.038(9)

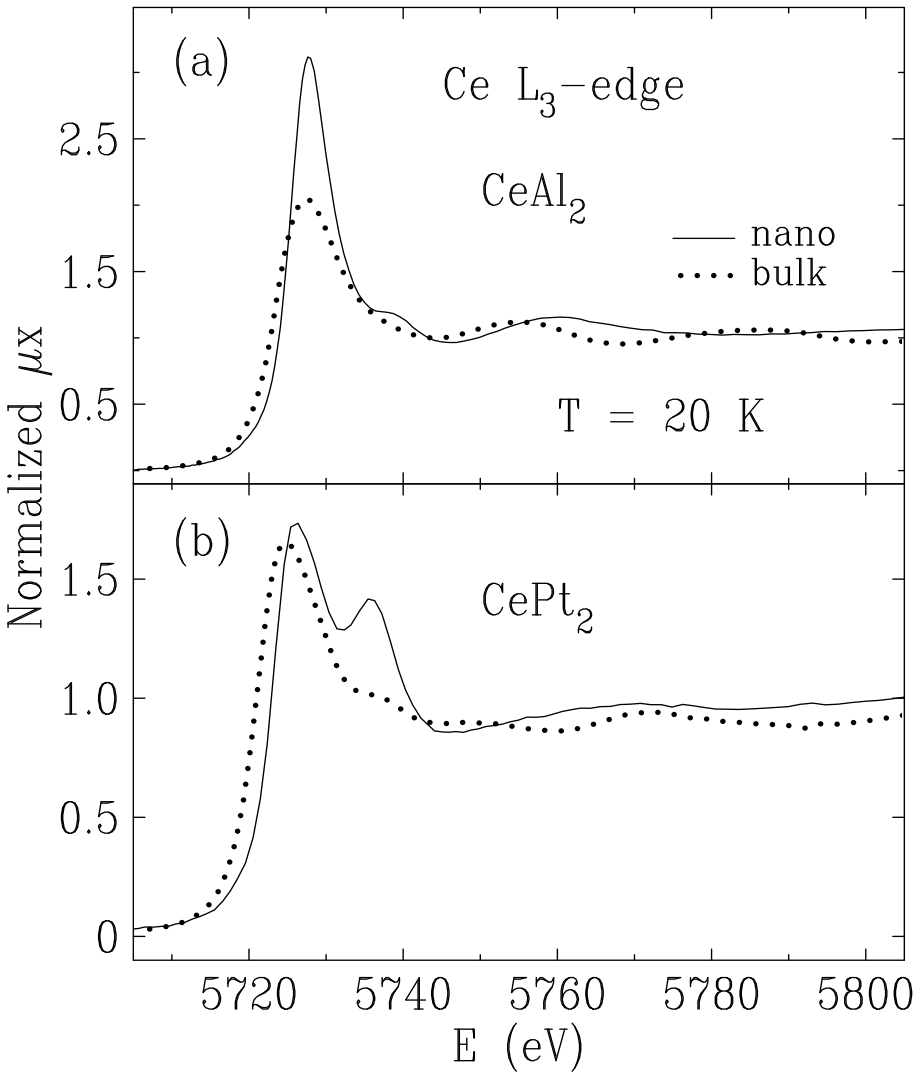

FIG. 1: Normalized total X-ray absorption as a function of incedent x-ray energy at Ce L_3-edge on $CeAl_2$ (a) and $CePt_2$ (b).

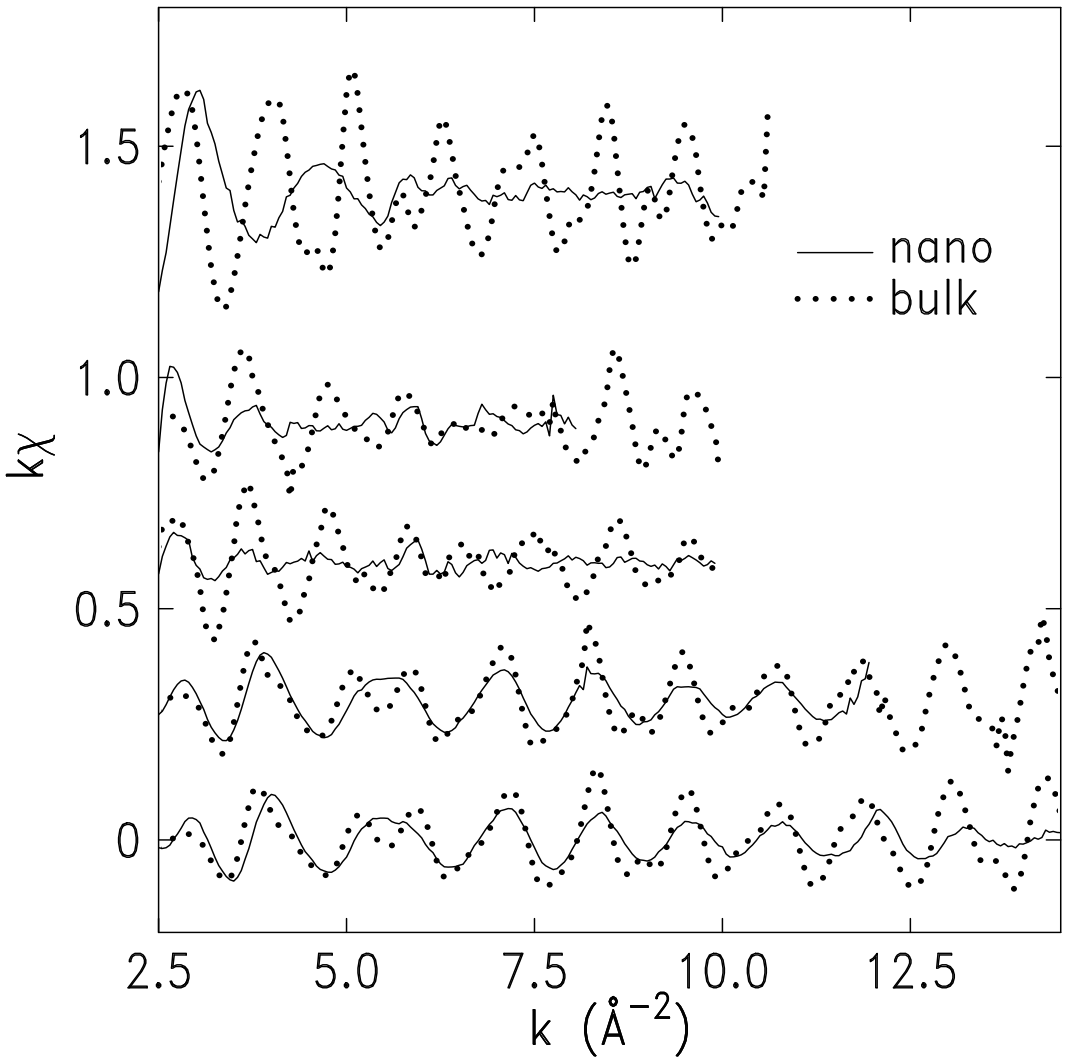

FIG. 2: XAFS ($k\chi$) as a function of wave number vector k measured at 20 K. From top, Ce L_3-edge on $CeAl_2$, $CePt_2$ and $CePt_{2.5}$, and Pt L_3-edge on $CePt_2$ and $CePt_{2.5}$. The XAFS data could not be obtained beyond $k = 10$ Å^{-1} at Ce L_3-edge due to the Ce L_2-edge.

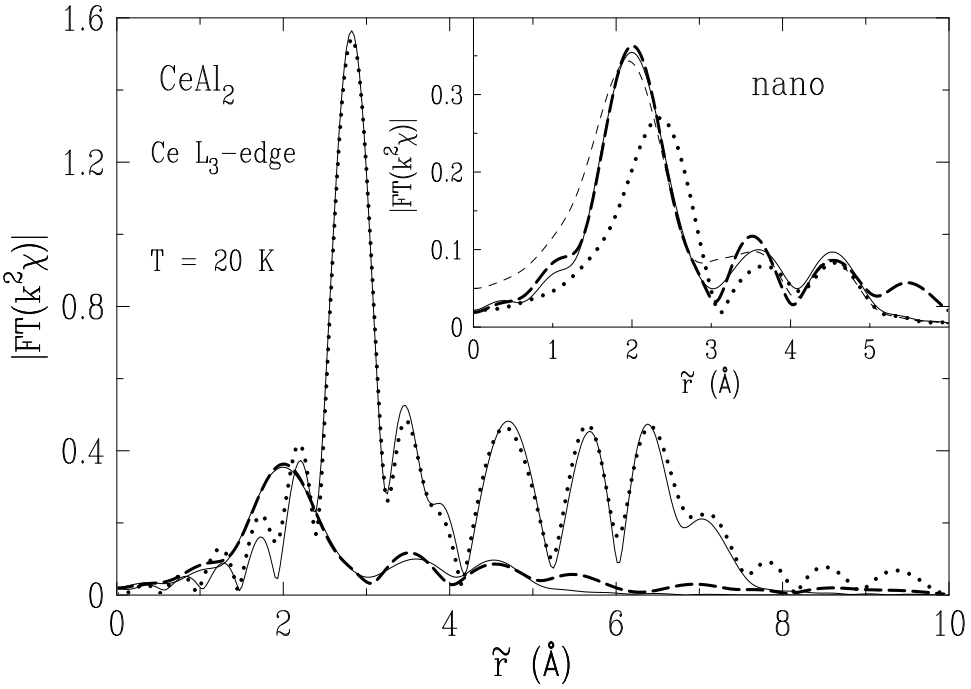

FIG. 3: Magnitude of Fourier transformed XAFS data from a bulk (dotted line) and a nanocrystal (thick-dashed line) of $CeAl_2$ as a function of distance from probe atom Ce. Solid lines are best fits. Inset indicates the XAFS data from the nanoparticle $CeAl_2$ and fits with the different models of Al-O mixed (solid line), Al only (dotted line) and O only (thin-dashed line).

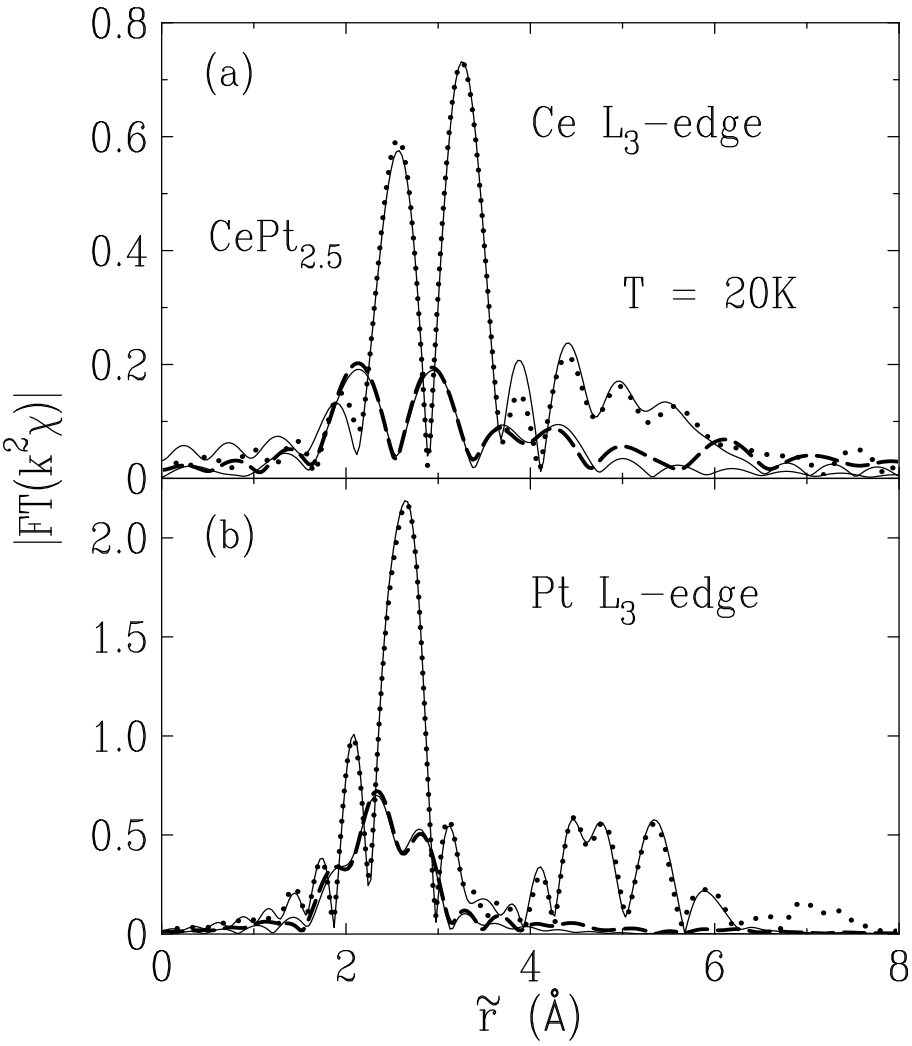

FIG. 4: Magnitude of Fourier transformed XAFS data from a bulk (dotted line) and a nanocrystal (thick-dashed line) of $CePt_{2.5}$ as a function of distance from probe atom Ce (a) and Pt (b). Solid lines are best fits.

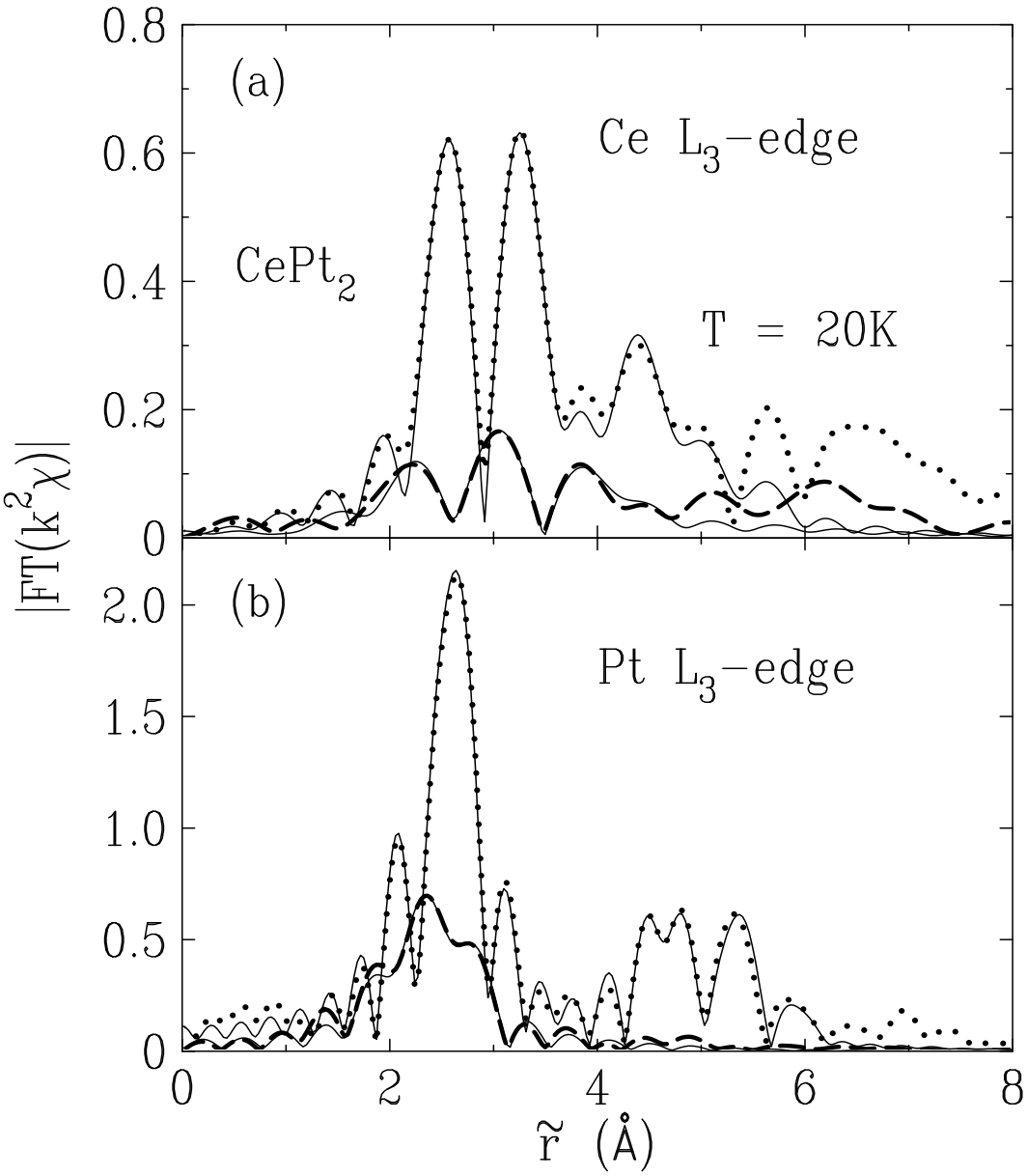

FIG. 5: Magnitude of Fourier transformed XAFS data from a bulk (dotted line) and a nanocrystal (thick-dashed line) of $CePt_2$ as a function of distance from probe atom Ce (a) and Pt (b). Solid lines are best fits.